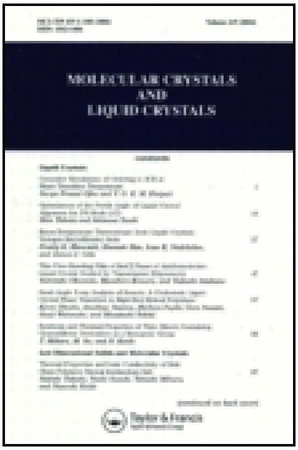

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Universality of the Critical Dynamics and the Nature of the Nematic-Isotropic Phase Transition

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Universality of the Critical Dynamics and the Nature of the Nematic–Isotropic Phase Transition

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The pretransition behaviour of the static and dynamic properties near the nematic–isotropic (N–I) phase transition are discussed in view of the last experimental investigations. In this case there are no simple power laws linked by universal relationships, as in the vicinity of a second-order phase transition.

The universal picture is restored if in place of $T-T^*$ (T^* is the absolute stability limit of the isotropic phase) we use the susceptibility for statics and the time of relaxation for dynamics as the scaling factor. The reconstructed universal picture allows one to match quantitatively the anomalies of equilibrium and dynamic properties. The universal scaling functions appear to have the Gaussian asymptotic behaviour. The physical reasons of such behaviour are also discussed.

Keywords: nematic–isotropic transition

I. INTRODUCTION

The phase transition from isotropic liquid to nematic liquid crystal (N–I) is a weak first order one. As a rule it is characterized by a small latent heat and by large pretransitional anomalies in a relatively wide temperature region, similar to those observed near a second order transition. The N–I transition is the simplest and the most studied of all phase transitions in liquid crystals. Therefore it is surprising that until now there are no clear answers to some key questions concerning the nature of this phenomenon. First of all it is not quite clear what makes this transition so weakly first order.

A generally accepted description of the N–I transition is based on the Landau–de Gennes phenomenological theory[1,2] with the nematic order fluctuation corrections in Gaussian approximation (see the review by Gramsbergen, Longa and de Jeu).[3] De Gennes[2] was the first to put forward the question of the validity of the mean-field approach to such systems with short range interactions.

On the other hand starting with early works by Stinson, Litster and Clark[4] and others[5,6] the departures from the simple Curie–Weiss law (e.g. the law predicted by the mean-field theory for the susceptibility) are known. More recent and more accurate measurements of susceptibility[7–12] and heat capacity[13–15] manifest evident departures from the mean-field predictions close to the N–I transition point. These anomalies are most significant if the distance between the N–I transition and the transition to a smectic phase is small. This fact was interpreted in terms of a coupling between the fluctuations of the transitional and orientational order.[16,17]

There is an obvious alternative reason for breaking up the simple power laws close to the transition point. Although the N–I transition is weak, it is not weak enough to neglect the influence of the third-order term in the Landau–de Gennes expansion on the temperature dependence of the thermodynamic quantities. The approach to the temperature of the susceptibility divergence (T^*) is limited (at least for thermotropic nematics) to the interval

$$t = \frac{T - T^*}{T^*} > \frac{T_{\mathrm{NI}} - T^*}{T^*} > 10^{-3} ,$$

where T_{NI} is the temperature of the N–I transition. It is not an asymptotic range for obtaining critical exponents. Moreover the effective (empirical) exponents are changing while T_{NI} is being approached. Indeed it might be a consequence of the change of the parameter T^* used for the extrapolation. This fact means the temperature scale in the case of the N–I transition is not the best one for evidencing the real nature of the critical behaviour.

Recently[18,19] it was demonstrated by the adjustment of static and dynamic properties, that the universal behaviour can be reconstructed if one transforms the scale from temperature to susceptibility (or to relaxation time for dynamics). The universal scaling functions appeared to have Gaussian asymptotic behaviour. Estimates of the Ginzburg criterion show that the critical domain is not accessible. The first order transition takes place before it.

II. PREDICTIONS OF THE LANDAU-DE GENNES THEORY

Detailed discussions of the Landau-de Gennes theory can be found in many places (see e.g., Refs. 2, 3 and 20). In this part the main predictions concerning the interpretation of some static properties will be recalled.

In the uniaxial nematic phase the expansion of the free energy can be written as

$$F - F_0 = \frac{1}{2}AQ^2 - \frac{1}{3}BQ^3 + \frac{1}{4}CQ^4 + \dots, \tag{1}$$

where F is a molar free energy in RT_{NI} units, Q is a modulus of the tensor order parameter.

The minimization of (1) yields the following solutions:

$$\begin{aligned} &Q = 0 && \text{(isotropic phase)}, \\ &Q = \frac{B}{2C}\{1 + (1 - 4AC/B^2)\}^{1/2} && \text{(uniaxial nematic phase)}. \end{aligned} \tag{2}$$

In the expansion (1)

$$A = at \qquad \left(t = \frac{T - T^*}{T_{\mathrm{NI}}}\right). \tag{3}$$

If B were absent, T^* would be the mean-field second-order transition temperature. Since $B > 0$, T^* is the (mean-field) absolute stability limit of the isotropic phase. It is of course different from the actual transition temperature, which is given by

$$T_{\mathrm{NI}} = \frac{T^*}{(1 - 2B^2/9aC)} \tag{4}$$

Similarly the order parameter at the transition point is

$$Q_{\mathrm{NI}} = \frac{2B}{3C} \tag{5}$$

At the absolute limit of stability of the isotropic phase ($T = T^*$), the order parameter is

$$Q^* = \frac{B}{C} \tag{6}$$

If the expansion up to fourth order is valid, there is a universal ratio between the order parameter at T_{NI} and T^*:

$$\frac{Q_{\mathrm{NI}}}{Q^*} = \frac{2}{3} \tag{7}$$

Note however that, if the first-order character is such that higher order terms in the expansion have to be kept, this ratio will no longer be universal.

The temperature of the absolute stability limit of the nematic phase is determined by the disappearance of the $Q = 0$ solution:

$$\begin{aligned} T^{**} &= T^* + T_{\mathrm{NI}}\frac{B^2}{4aC} = T_{\mathrm{NI}}\left(1 + \frac{B^2}{36aC}\right) \\ Q^{**} &= \frac{B}{2C} \end{aligned} \tag{8}$$

Contrarily to Q^*, Q^{**} is not directly accessible in experiments.

The temperature dependence of Q in the nematic phase is contained in (2) more explicitly (see Figure 1a):

$$\begin{aligned} Q &= \frac{B}{2C}\left[1 + \left(1 - \frac{4aC}{B^2}t\right)^{1/2}\right] \\ &= \frac{B}{2C}\left[1 + \frac{2(aC)^{1/2}}{B}\left(\frac{T^{**} - T}{T_{\mathrm{NI}}}\right)^{1/2}\right] \end{aligned} \tag{9}$$

The specific heat excess in the nematic phase is

$$C_p = aRQ\left(\frac{\partial Q}{\partial T}\right)_{\mathrm{P}} = R\frac{a^2}{2C}\left[1 + \frac{B}{2(aC)^{1/2}}\left(\frac{T^{**} - T}{T_{\mathrm{NI}}}\right)^{-1/2}\right] \tag{10}$$

Note the square root singularity, which is absent in the mean-field second order case (*Figure 1*b). The jump of the specific heat at T_{NI} is

$$\Delta C_p = R\frac{2a^2}{C} \tag{11}$$

i.e.: it is four times larger than at a second order transition. Note that it does not depend on B.

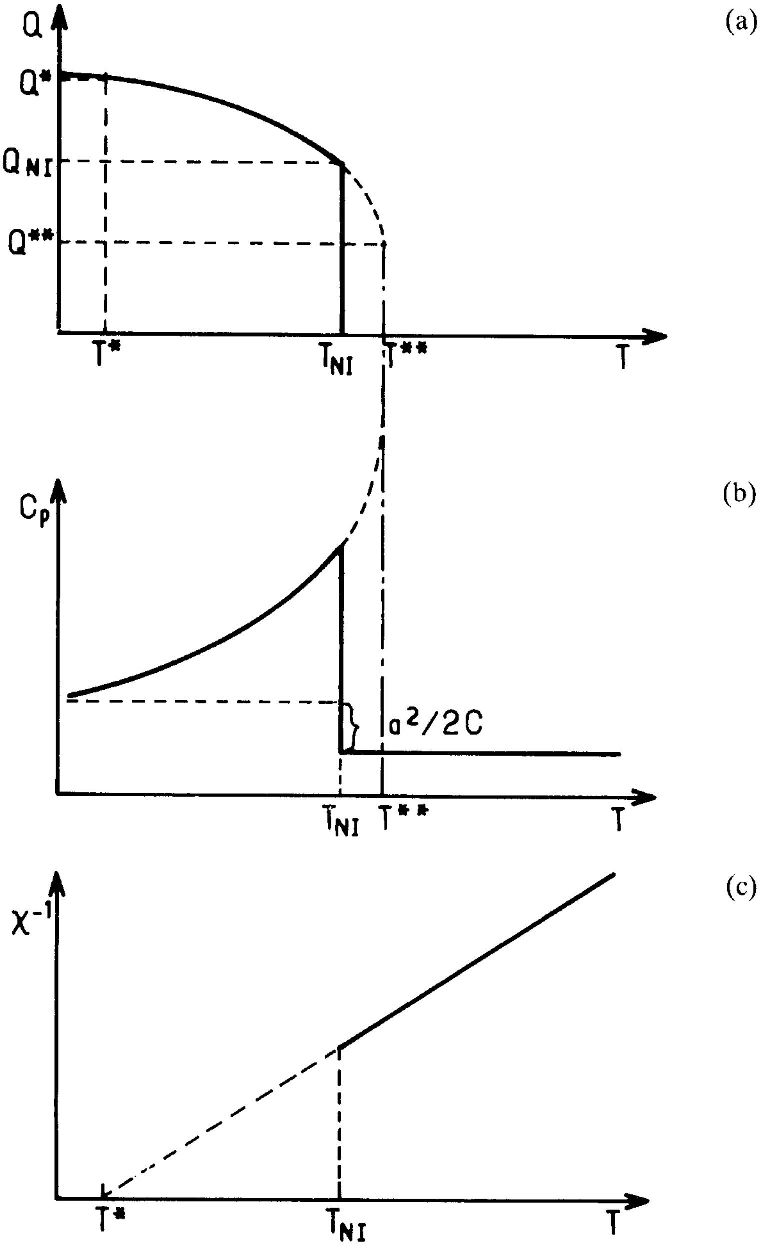

FIGURE 1 Predictions of the Landau–de Gennes theory: a) Order parameter, b) Specific heat, c) Susceptibility.

Similarly, the entropy, molar volume and enthalpy discontinuities (with obvious notations) are

$$\left.\begin{aligned} S_{\mathrm{I}} - S_{\mathrm{N}} &= \frac{1}{2} aQ^2_{\mathrm{NI}} R = \frac{2aB^2}{9C^2} R \\ V_{\mathrm{I}} - V_{\mathrm{N}} &= (S_{\mathrm{I}} - S_{\mathrm{N}}) \left(\frac{dP}{dT}\right)_{\mathrm{NI}} = \frac{2aB^2}{C^2} R \left(\frac{dP}{dT}\right)_{\mathrm{NI}} \\ H_{\mathrm{I}} - H_{\mathrm{N}} &= T_{\mathrm{NI}} (S_{\mathrm{I}} - S_{\mathrm{N}}) = \frac{2aB^2}{9C^2} RT_{\mathrm{NI}} \end{aligned}\right\} \tag{12}$$

In the isotropic phase the Curie–Weiss law for the susceptibility is valid (Figure 1c):

$$\chi^{-1} = \frac{\partial^2 F}{\partial Q^2} = a \frac{T - T^*}{T_{\mathrm{NI}}} \tag{13}$$

There are some physical reasons which yield renormalization of the coefficients in the Landau–de Gennes expansion.[20] There are molecular biaxiality which yields smaller values of B and molecular flexibility which renormalizes C. The biaxiality makes the first order nature of the transition weaker. The very soft chains of molecules might lead to very small values of C and make the situation close to a tricritical one. Finally, the fluctuation corrections should be taken into account.

III. RESULTS OF THE EXPERIMENTAL STUDY IN THE NEMATIC–ISOTROPIC BEHAVIOUR OF THE STATIC PROPERTIES

3.1. Order parameter

The temperature dependence of the order parameter in the nematic phase provides a first test for the validity of the Landau–de Gennes theory. The main experimental techniques and the corresponding measured quantities are four: i) optical (anisotropy of the refraction index),[21] ii) magnetic (anisotropy of the diamagnetic susceptibility),[22] iii) NMR (chemical shift and spin-lattice relaxation time),[23] iv) Raman spectroscopy (Raman depolarization ratio).[24]

The usual values of Q at the N–I transition temperature lie between 0.3 and 0.5. The uncertainty about Q_{NI} is usually large, due to the difficulty to extrapolate the data to the transition temperature and to the dependence of the result upon the technique used.[25] Noticeably, the value of Q_{NI} deduced from the birefringence of the sample can vary by up to a factor of 2 according to the chosen model for the local electric field. Anyway the large gap Q at the transition means that the coefficients B and C are of the same order of magnitude, in other words, that both B and C are small.

Fitting Formula (9) to the experimental temperature dependences of Q is made difficult by the fact that Q varies only weakly (~50%) within the nematic phase, a restriction which is the direct consequence of the large value of Q_{NI}. The more general form

$$Q = Q^{**} + k(T^{**} - T)^{\beta} \tag{14}$$

(with Q^{**}, T^{**}, k and β as adjustable parameters) can be successfully fitted to the experimental data for MBBA with $\beta = 1/2$,[26] the value expected from (9), as well as with $\beta = 1/4$ (tricritical value).[27]

A more stringent test of the Landau–de Gennes model is to compare the values of Q at T_{NI} and that at T^*. In any case the difference $Q_{NI} - Q^*$ is found of the order of a few percent instead of 50% as predicted by (7). This fact as well as the tricritical values of the effective exponent β in (14), obtained in many cases, can be easily explained by the smallness of the coefficient ($C \sim B << 1$). If C is small the fifth- and sixth-order terms in the expansion (1) must be taken into account. Thus the observable behaviour of $Q(T)$ is somewhat similar to the tricritical one.

3.2. Susceptibility

Measurements of the susceptibility χ are usually performed in the isotropic phase, where the Curie–Weiss law behaviour (13) is expected from the Landau–de Gennes theory. As pointed out by Lin Lei[28] the behaviour in the nematic phase is definitely less simple (no power law) due to the temperature dependence of the order parameter.

χ is the response of the medium to an external constraint which can be a magnetic field (Cotton-Mouton effect), an electrical field (Kerr effect) or an electrical field gradient (flexoelectrical coupling).[29] As a consequence of the fluctuation-dissipation theorem, χ can be obtained equivalently from the fluctuations of the anisotropy of the system around thermal equilibrium. The corresponding experimentally measurable quantity is the Rayleigh light-scattering cross section (in the limit of the zero wave vector). Up to now the most accurate results have been obtained by means of light-scattering (LS) and Cotton-Mouton effect (CME). The optical Kerr effect (OKE), or laser induced birefringence, should be most convenient for a simultaneous measurement of the susceptibility and of the coherence time of the fluctuations in a wide temperature range. However OKE has not yet been developed up to the same degree of accuracy and reliability as LS and CME.[29,30]

From most of the available experimental studies, a $(T-T^*)^{-1}$ type behaviour can be fitted roughly to the susceptibility variations in a wide although limited temperature range (measurements have been performed up to 40°C above the N–I transition temperature)[10-12] though the background scattering should be taken into account. However different experiments and techniques sometimes lead to discrepant values for the reduced transition temperature T_{NI}/T^*.

The departures from the Curie–Weiss law are observed systematically in the vicinity of T_{NI}. These departures are manifested usually by a bending down of the curve $\chi^{-1}(T)$[7-12] (Figure 2). The breakdown of the $(T - T^*)^{-1}$ type behaviour close to T_{NI} has been demonstrated with a large number of samples and techniques, in spite of some definite quantitative discrepancies regarding the amplitudes of these departures and the corresponding crossover temperature region (see also Refs. 31–34).

It is possible to explain the observed anomalies by the fluctuation corrections connected with the third-order term in the Landau–de Gennes expansion. Fan and Stephen[35] obtained the first fluctuation corrections to susceptibilty:

$$\chi^{-1} = at\left(1 + \frac{7CV_0}{2\pi^2 a^2 \xi_0^3}\, t^{-1/2} - \frac{7V_0 B^2}{4\pi^2 \xi_0^3 a^3}\, t^{-3/2}\right) \tag{15}$$

where ξ_0 is the bare correlation length (in mean-field approximation the correlation length $\xi = \xi_0 \cdot t^{-1/2}$), V_0 is a molecular volume (for MBBA $V_0 \simeq 470$ Å^3 for instance).

One can note that the correction connected with the third-order term in the Landau–de Gennes expansion is always negative. Furthermore Priest[36] showed that the coupling between uniaxial and biaxial fluctuations can also renormalize the coefficients of the Lan-

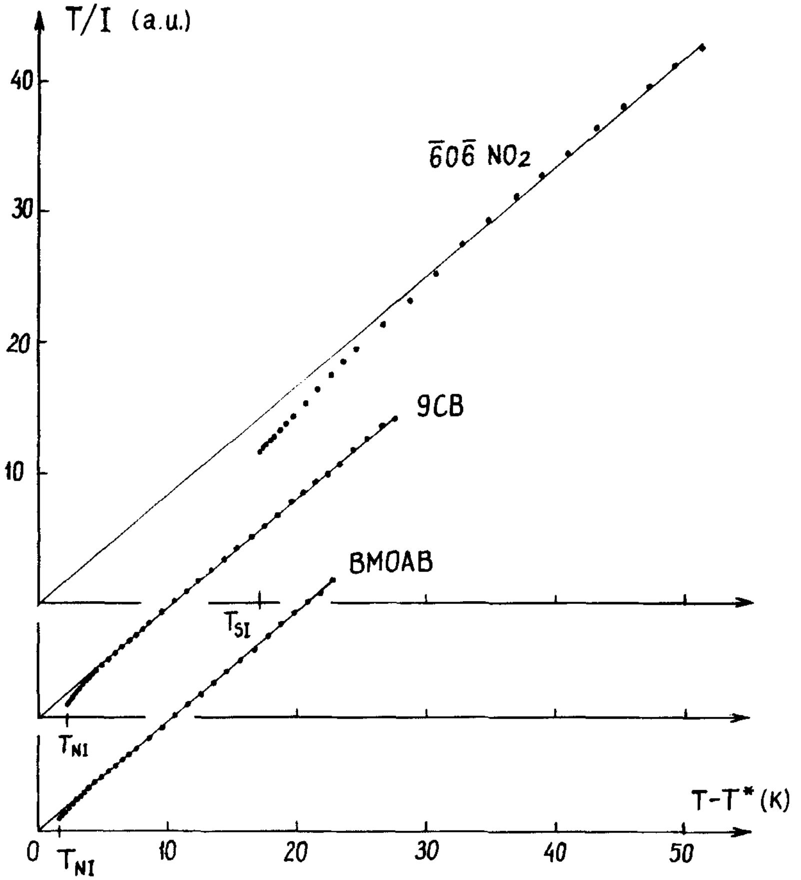

FIGURE 2 Inverse light-scattering intensity multiplied by temperature in the isotropic phase of some liquid crystals[12]: BMOAB has no smectic phase, $9CB$ has the 1, 9K nematic zone between isotropic and smectic A phase, $\overline{6}O\overline{6}NO_2$ has no nematic phase.

dau–de Gennes functional particularly provided smaller effective values of B.

An accurate calculation of the fluctuation corrections to susceptibility and heat capacity in the isotropic phase up to two loop order has been performed by Adzhemyan et al.[37] They obtain

$$\chi^{-1} = at\left[1 + Y_C t^{-1/2} - Y_B t^{-3/2} + Y_E - \left(\frac{1}{7}Y_C^2 - Y_{BD}\right)t^{-1}\ln t^{-1} - 25\left(63Y_B^2 t^{-3} + \frac{5}{14}Y_C Y_B t^{-2}\right)\right] \quad (16)$$

where Y_C, Y_B, Y_E, Y_{BD} are constants depending on the coefficients of the Landau–de Gennes expansion with keeping track of the fifth ($1/5\ DQ^5$) and sixth ($1/6\ EQ^6$) order terms. Of course when corrections begin to be sizeable, fifth and sixth order terms should be included. Thus one has too many coefficients to play with and it is easy to lose track of the physics of the problem. Indeed the Formula (15) and moreover the Formula (16) could be fitted to the experimental data for instance for MBBA and BMOAB.[37] Note, however, that recent independent systematic studies of series of smectogenic liquid crystals and their mixtures have shown evidently that the above mentioned departures are enhanced by the proximity of the smectic phases.[10,12] These facts were interpreted in terms of the cross coupling between positional and orientational ordering.[16,17] As a result the susceptibility in the isotropic phase is renormalized:

$$\chi^{-1} = a\frac{T - T^*_{\mathrm{NI}}}{T^*_{\mathrm{NI}}} + C_{\mathrm{NS}}\left[\frac{T - T^*_{\mathrm{SI}}}{T^*_{\mathrm{SI}}}\right]^{-1/2} - B^2_{\mathrm{NS}}\left[\frac{T - T^*_{\mathrm{SI}}}{T^*_{\mathrm{SI}}}\right]^{-3/2} \quad (17)$$

where C_{NS} and B_{NS} are proportional to the coupling (nematic–smectic) constants. T^*_{NI} and T^*_{SI} are the bare (in absence of the coupling) absolute stability limits of the isotropic phase for N–I and S–I transitions correspondingly. Note that the powers $-1/2$ and $-3/2$ are fundamentally different from those of Formula (15) (taking into account nematic fluctuations), which in fact under the same circumstances $+1/2$ and $-1/2$ respectively. As a result smectic fluctuations are more "dangerous."

Accurate measurements of the coherence length are very difficult because of its smallness ($\xi < 150$ Å) compared to visible wavelengths. The results obtained for MBBA by Gulari and Chu[9] are comparable with the prediction of the Landau–de Gennes theory, i.e. $\xi \sim (T - T^*)^{-1/2}$ with no restriction on the vicinity of the transition temperature. However the corresponding value of T^* differs definitely from that given by extrapolating linearly the high temperature part of $\chi\ (T)$ curve.

3.3. Heat capacity

The results of the early investigations[38,39] of the heat capacity anomaly near the N–I transition were so contradictory that sometimes they did not allow even a qualitative interpretation. It is well known now that the widely used technique of differential scanning calorimetry (DSC), being nonequilibrium, fails to separate correctly pretransitional effects in the anomaly of the heat capacity from a diffuse δ-function which is related to the latent heat.

It was the main reason for the erroneous consideration of the nematic–smectic A as a weak first transition while it was as a rule a second order one with a singular heat capacity.[40,41†] During last years more accurate (and chiefly closer to equilibrium) adiabatic calorimetry experiments in the vicinity of the N–I transition were carried out[13–15] and the situation has become clearer. The results of the specific heat measurements[13] of MBBA, BMOAB and MBBA + 3 molar % n-decane are shown on Figure 3. On Figure 4 the same results in the immediate vicinity of the transition point are represented.

These results can be understood taking into account the presence of not more than 1% impurities in the pure specimen. The character of the specific heat anomaly distortion in the impure specimen depends substantially on whether the impurities are in thermodynamical equilibrium or not. In absolutely pure and uniform specimens, δ-function for the specific heat corresponds to first order transition

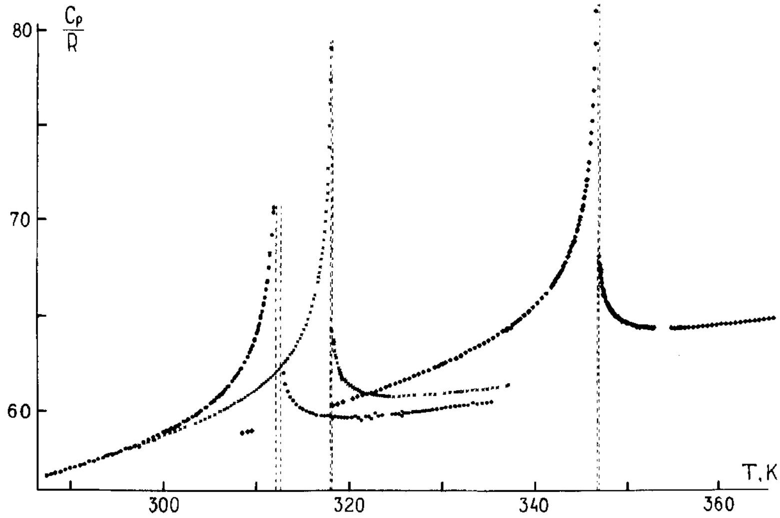

FIGURE 3 Specific heat in the vicinity of the N–I transition: ◆ BMOAB, × pure MBBA and ● MBBA + 3% n-decane.

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† See in Ref. 42 the discussion of this problem.

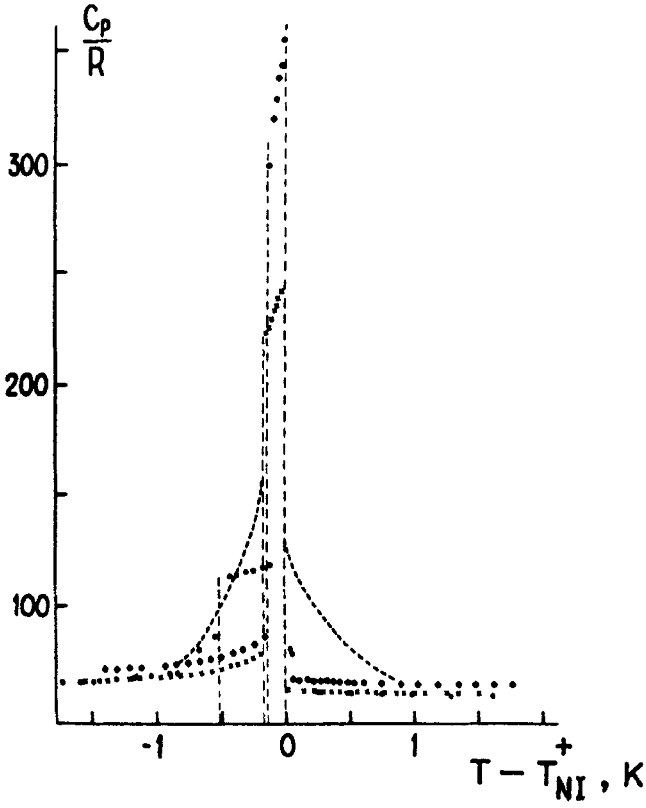

FIGURE 4 Specific heat in the immediate vicinity of the N–I transition. Notations are the same as in Figure 3.

points. The presence of a small amount of impurities in equilibrium converts the δ-function into a narrow trapezium, its width depending on the concentration of impurities. The area of this trapezium defines the latent heat of transition which was calculated to be $\Delta H/RT_{NI} = 0.102 \pm 0.001$ for MBBA and 0.110 ± 0.001 for BMOAB. Non-uniformly distributed out of equilibrium impurities distort the δ-function in another way. Each small section of the specimen has its own beginning and end of the transition depending on impurity concentration: the δ-function is smeared out. The results may be reproducible if the relaxation time of the inhomogeneity is much larger than the duration of a measurement. For instance the value of the N–I latent heat obtained by the DSC method[38] was twice the correct one.

The results of the measurements outside of the splitting region were fitted by the form

$$C_p/R = A_0\,(T/T^*)\,|t|^{-\alpha_{\rm eff}} + A_1 + A_2\,t + A_3\,t^2 \qquad (18)$$

and by the crossover formula:

$$C_p/R = (T/T^*)\,(B_1\,|t|^{1/2} + B_2\,|t|^{\alpha})^{-1} + B_3 + B_4 t + B_5 t^2 \qquad (19)$$

Both yield adequate fitting. The effective exponent $\alpha_{\rm eff}$ strongly depends on the range of fitting and has the value 0.3–0.4 for both substances in the nematic phase. Fixing $\alpha_{\rm eff}$ to the mean-field value 0.5 leads to an inadequate fitting.

In the isotropic phase because of the smallness of the anomaly the result of fitting strongly depends on whether the A_3t^2 term is included or not. When it is included one may obtain the adequacy at least for BMOAB, while fixing $\alpha_{\rm eff} = 0.5$ but the value $T - T^*$ appears to be only 0.13°C. The crossover Formula (19) also gives good fitting of the heat capacity in the nematic as well as in the isotropic phase if α is fixed for example to the value of 0.1. But the term $A_I t^{0.5}$ plays a dominant role. As in the previous case the adjusted value of $T - T^*$ is too small and in contradiction with the susceptibility measurements. One can see that the heat capacity behaviour is not simple and the obtained values of the critical exponents most probably are effective. Nevertheless if one tries to describe the nematic pretransitional behaviour using the expansion (1) one could come to the following values of the parameters similar for MBBA as well as for BMOAB.

Besides the anomalously small value of $T - T^*$ obtained from the heat capacity measurements there is an ever more important difference between the experiment and the calculations. There is no jump in the background part of the heat capacity while the theory [in the framework of the expansion (1)] predicts a jump $(a^2/2C) \simeq 10R$. The absolute experimental jump in the heat capacity $C_p^- - C_p^+ \approx 20R$ arises from the anomalous part of the heat capacity but according to the Formulas (10) and (11) it should be twice more. The agreement between the calculations and experiment can be improved taking into account the fifth- and sixth-order terms in the Landau–de Gennes expansion. It is understandable because the fourth-order coefficient C appears to be as small as the third-order coefficient B (see Table I). Therefore the so-called tricritical behaviour of the heat capacity[13] means only this fact.

TABLE I

The parameters of the Landau–de Gennes theory for MBBA

	Q_{NI}	H/RT_{NI}	$T_{NI} - T^*$ (K)	$T^{**} - T_{NI}$ (K)	A_0 ($\alpha_{eff}=0.5$)	a	B	C
Experiment	0, 4	0, 1	1–2 (susceptibility) 0, 13 (heat capacity)	0, 24	0, 68			
Calculations[a]			1, 9	0, 24	0, 8	1, 4	0, 06	0, 1

[a] Using the Formulas (4, 5, 8, 10, 12)

Using the values of the constant a, B and C given in Table I and taking into account the sixth-order term in the expansion (1) one can sufficiently improve the description of the heat capacity in the nematic phase and eliminate the jump ~10R in the background. To determine the sixth-order coefficient E the amplitude of the anomalous part of C_p was used as an additional initial parameter. The best value of E appears to be 0.33.†

If for the pretransitional part of the heat capacity in the isotropic phase the exponent α_{eff} is fixed on the mean-field value of $\alpha = 0.5$ one can calculate the bare coherence length ξ_0 [see Formula (47)]. It appears to be 5.6 A which is in good agreement with the results of the light scattering measurements ($\xi_0 = 6 \pm 1$ Å if one chooses $\nu = 0.5$ and $\alpha = 0.5$). As a matter of fact one can determine the mean-field value $\nu = 0.5$ and $\alpha = 0.5$ with the same accuracy as for the Curie–Weiss law of susceptibility. Both of them are not punctual and the scaling relation $2 - \alpha = 3\nu$ is not satisfied. At the same time the fundamental relation between the susceptibility and the heat capacity[43,44] appears to be justified (see Figure 5).

$$\delta C_p = (nRT^2V_0a^{3/2}/16\pi\ \xi_0^3)\ (\partial\chi^{-1}/\partial T)^2\ \chi^{1/2} \qquad (20)$$

where n is a number of fluctuating modes, $n = 5$ in the isotropic phase.

The relation (20) remains true even in the scaling theory if one neglects the deviations in the correlation function from Ornstein–Zernike form. In fact the Formula (20) can be considered as an equation of state in the isotropic phase.

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†The fifth-order coefficient D was assumed to be equal to zero.

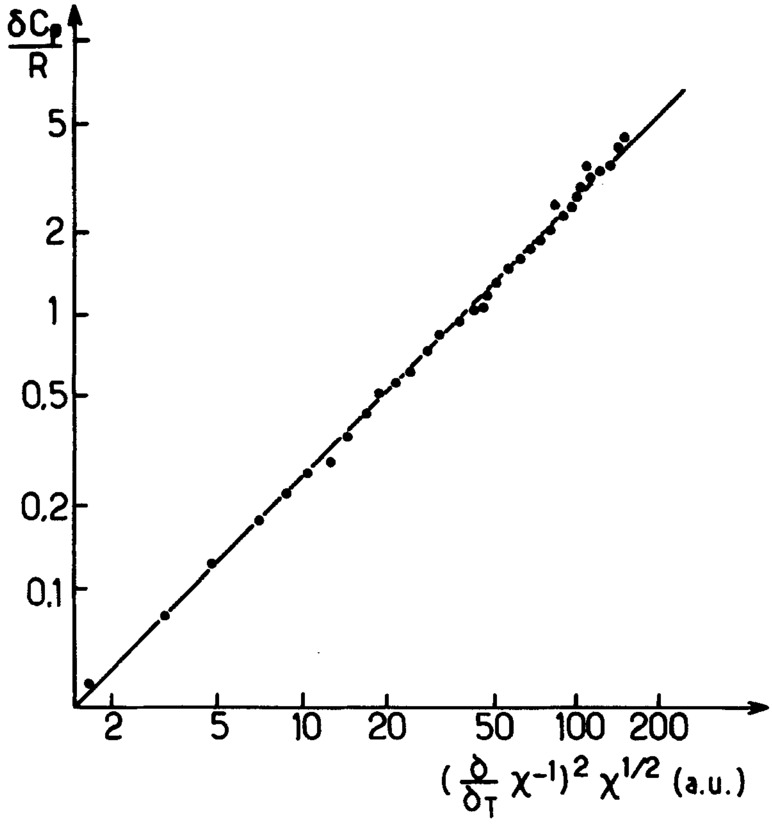

FIGURE 5 Test of the relation between excessive specific heat and susceptibility in the isotropic phase of BMOAB.

Thus one can see that the Landau–de Gennes theory even with fluctuation corrections can provide only a qualitative description of the experiment. The set of the constants which is the best for the heat capacity description is not appropriate for the order parameter (Q_{NI}/Q^* is too large). In any case near the I–N transition $CQ^4 \sim EQ^6$, i.e. the experimental temperature interval is in the range of the crossover from the tricritical-like to the critical or to the usual mean-field behaviour.

Probably near the I–N transition all the terms of the Landau–de Gennes expansion beginning from BQ^3 (and the corresponding fluctuation corrections) have the same order of magnitude. Therefore to coordinate all the physical properties one must use such a great number of the expansion terms that the description becomes unphysical.

IV. UNIVERSALITY OF THE CRITICAL DYNAMICS NEAR THE N–I PHASE TRANSITION

4.1. Sound absorption and dispersion are homogeneous functions

The N–I phase transition belongs to a dynamic universality class different from that relevant to critical points in fluids. The nematic order parameter is not conserved. The characteristic relaxation time depends on the susceptibility χ and effective "viscosity" η:

$$\tau = \chi\eta \tag{21}$$

while in fluids the critical relaxation time depends on the space scale:

$$\tau_q^{-1} = 2Dq^2 \tag{22}$$

(q is a wave vector).

Recently the nature of the critical dynamics near the I–N transition was cleared up in details with the help of acoustic relaxation investigations.[18,19] A quantitative agreement between dynamics and statics was shown to hold. It is remarkable that no assumptions connected with the nature of pretransitional behaviour of the equilibrium properties were used. In particular the temperature of the susceptibility singularity T^* was never used as an adjustable parameter. The following questions were posed:

i) Are there homogeneous functions of variables ω (frequency) and τ (relaxation time) which describe the acoustic relaxation in the isotropic as well as in the nematic phase?

ii) Have these functions (if they exist!) a universal form?

iii) What restrictions to the transitional behaviour of the statics are imposed with the universality of the dynamics?

Two substances were investigated, MBBA and BMOAB, because accurate heat capacity measurements were performed for them previously. Both the excess sound absorption and sound velocity dispersion were found to be homogeneous functions of ω and τ in the isotropic as well as in the nematic phase (Figure 6 and Figure 7).

$$1 - (u/u_\infty)^2 = A(\tau)\varphi_1(\omega\tau) \tag{23}$$

$$\alpha'\lambda = \pi A(\tau)\varphi_2(\omega\tau) \tag{24}$$

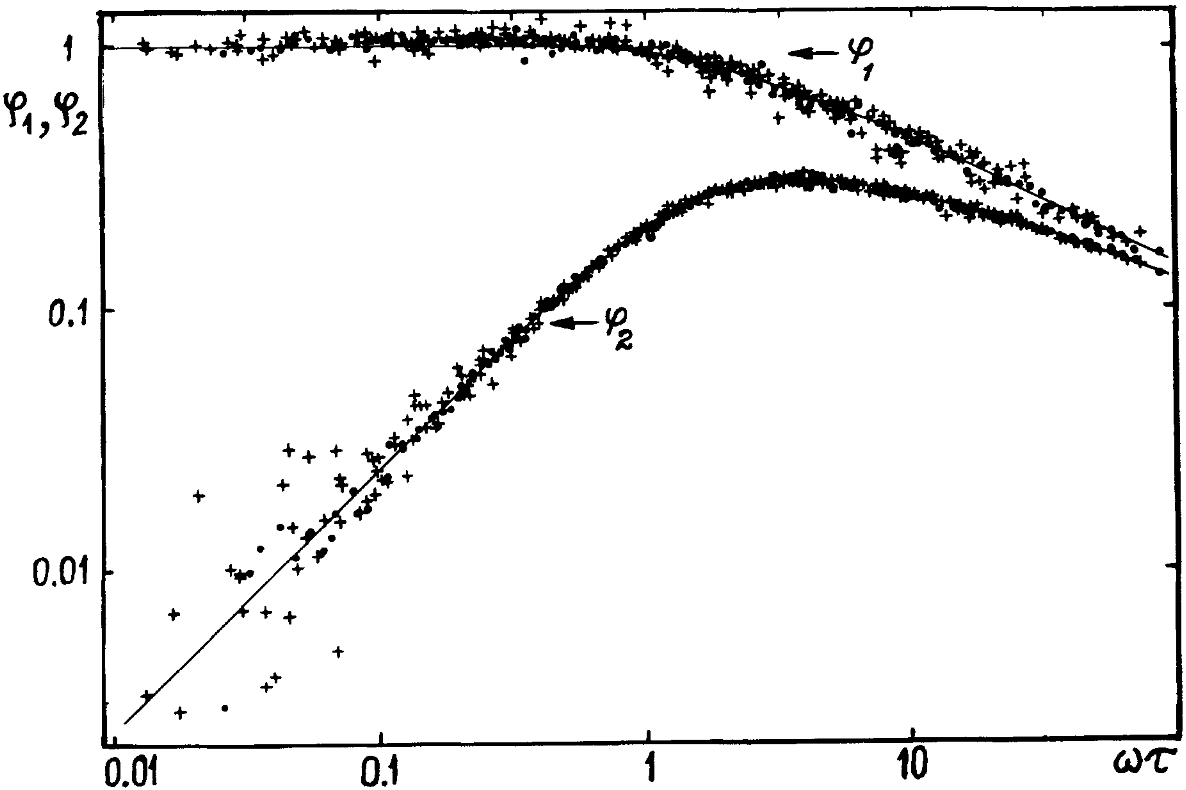

FIGURE 6 Universal functions φ_1 and φ_2 for the isotropic phase of MBBA (circles) and BMOAB (crosses). The continuous curves represent the Imura–Okano functions (Eq. 45).

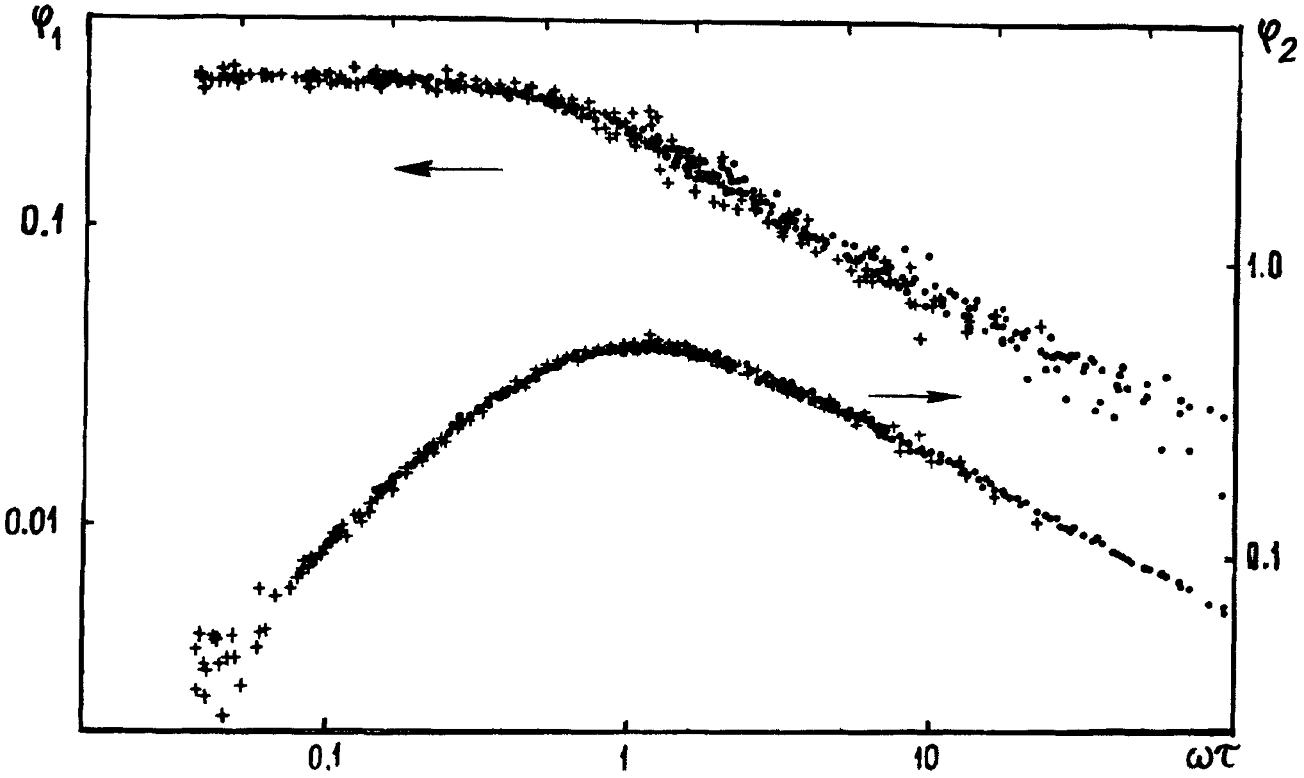

FIGURE 7 Universal functions φ_1 and φ_2 for the nematic phase of MBBA (circles) and BMOAB (crosses). The scales for φ_1 and φ_2 are shifted relative to one another to avoid crossing.

where u_∞ is the velocity of sound extrapolated to $\omega \rightarrow \infty$, it is a regular function, λ is the sound wave length. The dispersion of sound velocity and the absorption are determined by the real and imaginary parts of the complex adiabatic compressibility $\tilde{\beta}_s$

$$\tilde{u}^2 = u_\infty^2 - \Delta\tilde{u}^2 \tag{25}$$

where

$$\tilde{u}^2 = (\rho\tilde{\beta}_s)^{-1}$$

$$\mathrm{Im}\,(\Delta\tilde{u}^2/u_\infty^2) = \alpha'\lambda/\pi \tag{26}$$

$$\mathrm{Re}\,(\Delta\tilde{u}^2/u_\infty^2) = 1 - (u/u_\infty)^2 \tag{27}$$

In the nematic phase the pretransition absorption and dispersion are determined by at least two mechanisms: the relaxation of the order parameter and the relaxation of the order parameter fluctuations. In the isotropic phase only the fluctuation mechanism exists.

4.2. Mean-field approximation

In the mean-field approximation

$$\Delta\tilde{u}^2\,(\omega\tau) = A_1(T)\,F_1(x) + A_2(T)\,F_2(x) \tag{28}$$

where $x = i\omega\tau$

$$F_1(x) = (1 + x)^{-1} \tag{29}$$

$$F_2(x) = (x/2)^{-1/2}\,(2/x - 1)^{1/2} - (2/x)^{1/2} \tag{30}$$

$$A_1(T) = (\partial P/\partial Q)_S\,(\partial Q/\partial\rho)_S \tag{31}$$

$$A_2(T) = 1/32\pi(\partial^2 P/\partial Q^2)_S(\partial\chi^{-1}/\partial\rho)_S\,\frac{V_0}{\xi_0^3}\,\chi^{1/2} \tag{32}$$

The approximate expressions of $A_1(T)$ and $A_2(T)$, if calculated with the Landau–de Gennes expansion (1), have the form

$$A_1(T) = \frac{\partial Q}{\partial T}\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial Q}\right) \tag{33}$$

$$A_2(T) = g\left[\frac{\partial}{\partial T}(\chi^{-1})\right]^2 RT(\chi^{-1}a^{3/2})^{-1/2}\frac{V_0}{32\xi_0^3} \qquad (34)$$

where g is a constant.

The first term in the expression (28) is connected with the relaxation of the parameter,[45] the second is connected with the relaxation of the correlation function and proportional to the fluctuation part of the heat capacity.[46] The conditions of the homogeneity are satisfied only if the temperature dependence of the functions $A_1(T)$ and $A_2(T)$ is identical. It is easy to see that the forms of the functions $A_1(T)$ and $A_2(T)$ are determined by the fine interplay of the coefficients of the expansion (25). The identical temperature dependence of $A_1(T)$ and $A_2(T)$ exists only with a special choice of the values of the coefficients (e.g. $B = C = D = 0$). An attempt was made to bring the acoustic and calorimetric data to coincidence in the nematic phase of MBBA using just the same set of the coefficients of the expansion (1) with account of the sixth-order term ($\frac{1}{6}EQ^6$): $a = 1.4$, $B = 0.06$, $C = 0.1$, $D = 0$, $E = 0.33$, $\xi_0^2 = 36\text{Å}$.[2] One can see on Figure 8 that the violation of the homogeneity is small and in general is of the same order of magnitude as the error of the description of the equilibrium properties. Perhaps taking into account the next terms of the perturbation and varying the new adjustable parameters one can succeed to bring into agreement quantitatively all the experimental data including the temperature dependence of the order parameter. But this way seems to be rather artificial and at least impractical.

It is not likely that the homogeneity found experimentally for the two substances, which is indeed a universal property of the N–I transition, is the result of a random (and fairly fine) interplay of constants. Moreover, it is worth noting the large value of the fluctuation contribution to the properties of the nematic phase: A_2/A_1 varies from 0.2 for $T_{\mathrm{NI}} - T = 15\mathrm{K}$ to 0.33 for $T_{\mathrm{NI}} - T = 0.1\mathrm{K}$. At high frequencies the fluctuation mechanism is practically the only one, because $\lim_{x\to\infty} F_1(x) \sim x^{-1}$ and $\lim_{x\to\infty} F_2(x) \sim x^{-1/2}$.

4.3. Dynamic scaling

A more natural representation of the experimental results can be obtained in the scaling form[47]:

$$\Delta\bar{u}^2/u_\infty^2 = \tau^y\Psi(x) \qquad (35)$$

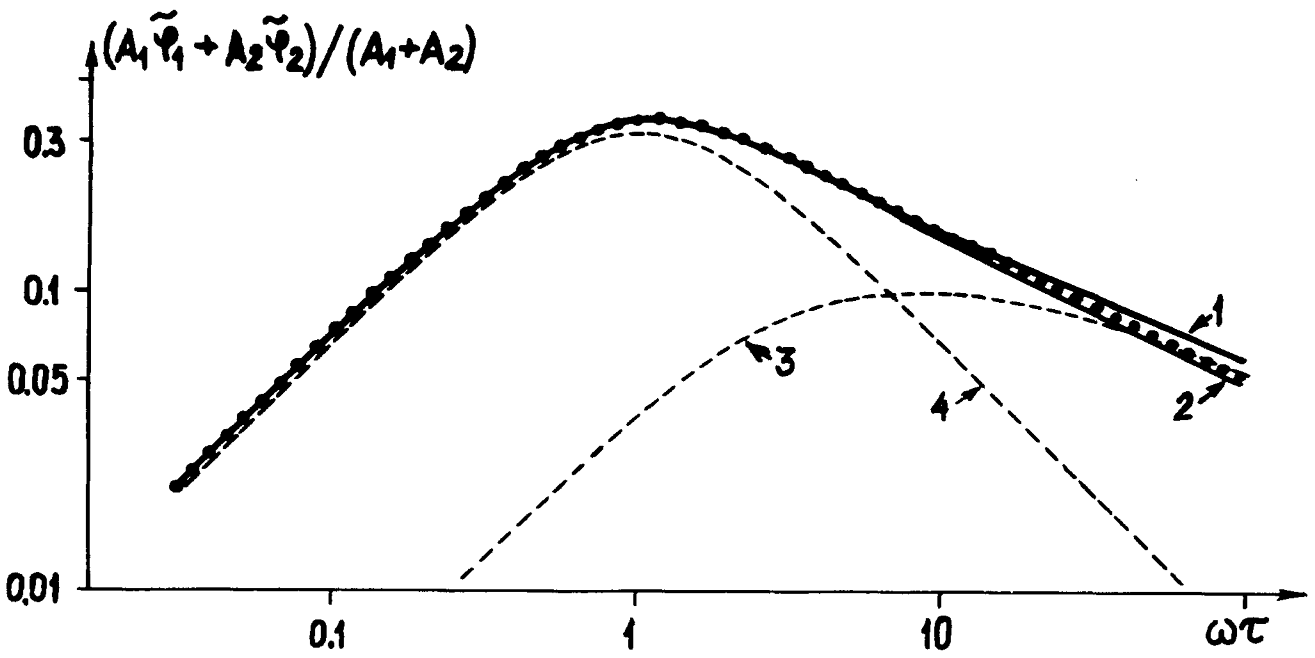

FIGURE 8 Results of a calculation of the absorption coefficient of the nematic phase of MBBA, carried out in the mean-field approximation using Eqs. (28–34) (here $\tilde{\varphi} = \mathrm{Im}F_1, \tilde{\varphi}_2 = \mathrm{Im}F_2$): 1) $T_{NI} - T = 0.1$ K; 2) $T_{NI} - T = 1.0$ K; 3) $A_2 \cdot \mathrm{Im}F_2$ (for $T_{NI} - T = 0.1$ K); 4) $A_1 \cdot \mathrm{Im}F_1$ (for $T_{NI} - T = 0.1$ K). The points are the average experimental values.

where

$$y = \alpha/z$$

α and z are the critical exponents of the heat capacity and relaxation time correspondingly.

In the hydrodynamic regime ($x << 1$)

$$\Psi(x) = \Psi(0) + \Psi'(0)u + 1/2\,\Psi''(0)x^2 + \ldots$$

$$(u^2{}_\infty - u^2)/u^2_\infty = \mathrm{Re}\,(\Delta\tilde{u}^2/u_\infty) = \tau^y\left[\Psi(0) - \Psi''(0)\frac{\omega\tau}{2}\right] \tag{36}$$

$$\frac{1}{\pi}\alpha'\lambda = \mathrm{Im}\,(\Delta\tilde{u}/u_\infty) \approx \tau^y\,\Psi(0)\,\omega\tau \tag{37}$$

In the critical regime ($x >> 1$)

$$\Psi(x) = A_\infty x^{-y} \tag{38}$$

$$(u^2_\infty - u^2)/u^2_\infty = A_\infty \omega^{-y}\cos(\pi y/2) \tag{39}$$

$$\alpha'\lambda/\pi = A_\infty\,\omega^{-y}\sin(\pi y/2) \tag{40}$$

One can see that according to dynamic scaling the asymptotic behaviour of the absorption and dispersion in the hydrodynamic as well as in the critical regime is determined by the same critical exponent y and in the limit the relation of the dispersion to the absorption tends toward constant value:

$$\begin{aligned}(u^2_\infty - u^2)/u^2_\infty\,\alpha\lambda &= \mathrm{Re}\,\Psi(x)/\mathrm{Im}\,\Psi(x)\\ &= \varphi_1(\omega\tau)/\varphi_2(\omega\tau) = \mathrm{ctg}\,(\pi/2)y\end{aligned} \tag{41}$$

One can see in Figures 6 and 7 that both predictions of the scaling theory are justified. The value of the critical exponent y is near the mean-field result $y = 0.5$. The value of the ratio is $\varphi_1/\varphi_2 = 1 \pm 0.2$ for both substances in both phases. It is remarkable that the experimental value $y \approx 0.5$ is near the mean-field prediction while the pretransition behaviours of both the heat capacity and the susceptibility do not have the pure mean-field exponents. The values of the critical exponents demand the adjustable parameter T^* for the extrapolation and can be considered to be effective but not true. Only the choice of the relaxation time as a scale instead of the temperature leads to the discovery of the true exponent behaviour.

The scaling description seems to be attractive in that at least it allows to avoid the large amount of adjustable parameters of the expansion (1) with accounting the higher-order terms. If one supposes that the effective "viscosity" in (21) has the same temperature dependence as the shear viscosity:

$$\eta = \eta_0 \exp(\theta/T) \qquad (42)$$

where $\theta = 4200\text{K}$, then the relaxation time calculated from the Formula (21) using light-scattering data is in good agreement with independent experiments in MBBA.[48]

The pretransitional amplitudes of the absorption and dispersion appeared to be proportional to the pretransitional amplitude of the heat capacity. Moreover the coefficient of proportionality is close to one. The value of the ratio

$$g = A(T)\,(C_p)_0/\delta C_p \qquad (43)$$

[$(C_p)_0$ is a regular part of the heat capacity] was calculated by Imura and Okano[46] who following Fixman[43] proposed the identical anomalous parts in the heat capacities at constant pressure C_p and constant volume C_V. It corresponds to the neglect of the dependence of the transition temperature on pressure.[49] Taking into account in first approximation of the pressure dependence of T_{NI} gives

$$g = (\gamma_0 - 1) + 2\gamma_0(\partial P/\partial T)_v(dT_{\text{NI}}/dP) \qquad (44)$$

Using the experimental values of the parameters in Eq. (44) [$(\partial P/\partial T)_V \approx 1\ MPa/\text{K}$, $\gamma_0 = (C_p)/(C_V) \approx 1.2$ $(dT_{\text{NI}}/dP) = 0.35\text{K}/MPa$] one can obtain the estimate (with accuracy 10–20%) $g \approx 1$ in an agreement with the experiment.

In the isotropic phase the universal functions $\varphi_1(\omega\tau)$ and $\varphi_2(\omega\tau)$ follow the prediction of Imura–Okano theory based on the Ornstein–Zernike approximation.

$$\varphi_1(\omega\tau) = \mathrm{Re}\, F_2(x) = \left(\frac{4}{\omega\tau}\right)^{1/2} \left[\frac{2}{\omega\tau} + \left(1 + \frac{4}{\omega^2\tau^2}\right)\right]^{-1/2}$$

$$\varphi_2(\omega\tau) = \mathrm{Im}\, F_2(x) \left(\frac{4}{\omega\tau}\right)^{1/2} \left\{\left[\frac{2}{\omega\tau} + \left(1 + \frac{4}{\omega^2\tau^2}\right)^{1/2}\right]^{1/2} - \left(\frac{4}{\omega\tau}\right)^{1/2}\right\} \quad (45)$$

In the nematic phase the universal functions $\varphi_1(\omega\tau)$ and $\varphi_2(\omega\tau)$ can be presented by the following linear combinations of F_1 and F_2:

$$\varphi_1(\omega\tau) = m\, \mathrm{Re}\, F_1(x) + (1 - m)\, \mathrm{Re}\, F_2(x)$$

$$\varphi_2(\omega\tau) = m\, \mathrm{Im}\, F_1(x) + (1 - m)\, \mathrm{Im}\, F_2(x) \quad (46)$$

where $m = 0.75$. The value of m is close to the results of the calculations in the mean-field approximation but does not depend on the proximity of the transition point. It means the identical temperature dependence of the amplitudes A_2 and A_2 in the Formula (30) and this is an additional argument for using of the scaling approach. This scaling approach is compatible with the mean-field (better to say Gaussian) dynamic exponent $y = 0.5$.

One can remark that the asymptotics of the dynamic scaling functions allow to make a conclusion about the nature of the order parameter dynamic universality class. For conserved order parameter (density or concentration) $y = \alpha/(2 - \alpha)$. Indeed for investigated critical fluids[49] $\alpha \approx 0.11$ and $y \approx 0.06$ while in Gaussian approximation $\alpha = 0.5$ and $y = 1/3$. Nematic order parameter is not conserved, so $y = \alpha/z$. In Gaussian approximation $\alpha = 0.5$, $z = 1$ and $y = 0.5$.

V. CONCLUSION

The following question might be raised: what physical reasons make the scaling approach to be compatible with the Gaussian dynamic behaviour. The full answer is yet unknown. However some speculations can be given. The first fluctuation correction to the specific heat in the isotropic phase is

$$\frac{\delta C_p}{R} = \frac{V_0}{16\pi\xi_0} t^{-1/2} \quad (47)$$

This formula can be obtained from the relation (20) if one assumes $\chi = at$.

Comparing the part of the specific heat due to fluctuations with the mean-field discontinuity at the transition point $[\Delta C_p = (a^2/2C) R]$ yields an expression of the Ginsburg criterion. Mean-field will be valid provided if

$$t >> Gi = \frac{n^2}{64\pi^2} \frac{C^2}{a^4} \left(\frac{V_0}{\xi_0^3}\right)^2 \tag{48}$$

In the isotropic–nematic case, we have $n = 5$, $n^2/64\pi^2 \approx 0.04$, $(V_0/\xi_0)^2 \approx 4 - 5$.

If one assumes $a \approx C \approx 1$, the critical regime should be expected, since

$$Gi \approx 0.2$$

while

$$\frac{T_{\mathrm{NI}} - T^*}{T_{\mathrm{NI}}} \approx 10^{-3} - 10^{-2}$$

However, as experiments show the fourth-order coefficient $C \approx 0.1$ (i.e. it is in fact as small as B). Hence the true value of the Ginsburg number is:

$$Gi \approx 2 \cdot 10^{-3}$$

and the critical domain $t << Gi$ is not accessible. The same result (with the accuracy of numerical factor) one can obtain comparing the second term in brackets of Formula (15) with unit. The other Ginsburg criterion which takes into account the fluctuation correction connected with cubic invariant in free energy expansion can be obtained by comparing the B^2 term in Formula (15) with unit. The mean-field approach is allowed in the range

$$t >> Gi = \left(\frac{7B^2}{4\pi^2 a^3} \frac{V_0}{\xi_0^3}\right)^{2/3} \approx 5 \cdot 10^{-3}$$

It is remarkable the both estimates are the same order of magnitude as well as the value $(T_{\mathrm{NI}} - T^*)/T_{\mathrm{NI}} \approx 3.10^{-3}$ and the critical domain is not yet achieved though the fluctuation corrections are significant. One can note that the anomalous small values of the coefficients C

and B provide the small values of the Ginsburg criterions in spite of short-range molecular forces ($V_0/\xi_0^3 \gg 1$). In spite of the relatively small value of the Ginzburg number the mean-field universality is broken up by the fluctuation corrections. Using the scaling approach we take into account the fluctuations in general and hence reconstruct the universality.

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